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Key Points:
- Comparison of high-temporal resolution multiproxy records of particulate pyrogenic carbon (PyC) in aquatic sediments
- Records of combustion are clearly decoupled in the (pre-)industrial era
- Aquatic sediments chronicle local and regional sources of combustion

Supporting Information:
- Supporting Information S1

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Decoupled sedimentary records of combustion: Causes and implications

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Abstract Pyrogenic carbon (PyC) is a collective term for carbon-rich residues comprised of a continuum of products arising from biomass burning and fossil-fuel combustion. PyC is ubiquitous in the environment where it can be transported by wind and water before being deposited in aquatic sediments. We compare results from four different methods used to trace PyC that were applied to a high-temporal resolution sedimentary record in order to constrain changes in PyC concentrations and fluxes over the past ~250 years. We find markedly discordant records for different PyC tracers, particularly during the preindustrial age, implying different origins and modes of supply of sedimentary PyC. In addition to providing new insights into the composition of sedimentary combustion products, this study reveals that elucidation of past combustion processes and development of accurate budgets of PyC production and deposition on local to regional scales requires careful consideration of both source characteristics and transport processes.

1. Introduction

Pyrogenic carbon (PyC), including charcoal and soot-like materials, is formed during the incomplete combustion of biomass or fossil fuels and largely consists of condensed polyaromatic structures [*Antal and Grønli*, 2003; *Bird et al.*, 2015]. The cluster size of PyC increases with temperature, with relative small aromatic domains (≤7 rings) at low production temperatures (<400°C) and highly condensed domains (>19 rings) at higher temperatures (700°C) [*McBeath et al.*, 2011] depending on oxygen availability and reaction times [*Bockhorn*, 1994]. Low molecular weight carbon compounds can be building blocks for formation of soot particles [*Pöschl and Shiraiwa*, 2015].

PyC is a key component of the global carbon cycle due its slow intrinsic decomposition rate and its ubiquity in the environment [*Bird et al.*, 2015; *Goldberg*, 1985; *Schmidt and Noack*, 2000]. PyC originates from wildfires, land clearance, and energy production and from burning of fossil fuel in industry and transportation [*Bond et al.*, 2013; *Goldberg et al.*, 1981; *Thevenon et al.*, 2010]. PyC can subsequently be retained in soils, where it has been reported to account for between <1 and 60% of total organic carbon (TOC) [*Preston and Schmidt*, 2006], or transported over large distances by wind and water, eventually accumulating in aquatic sediments [*Bird et al.*, 2015]. Riverine transport alone is estimated to transfer 19–80 Tg yr^{-1} of particulate PyC from terrestrial to marine systems [*Bird et al.*, 2015; *Dittmar et al.*, 2012; *Gustafsson and Gschwend*, 1998; *Jaffé et al.*, 2013; *Sánchez-García et al.*, 2013]. However, data for lacustrine and estuarine systems remain scarce despite their potential importance as a long-term sink for PyC [*Bird et al.*, 2015; *Thevenon et al.*, 2010]. This information void needs to be filled before modern-day PyC budgets can be calculated and past PyC production and cycling assessed. To address the latter, sedimentary sequences, which integrate signals derived from small catchment areas, can yield detailed records of PyC production and deposition that can be linked to local land use history. *Lima et al.* [2003], for example, developed a detailed record spanning the nineteenth and twentieth centuries of combustion-derived polycyclic aromatic hydrocarbons (PAH) from Pettaquamscutt River basin sediments and interpreted PAH fluxes in the context of the history of fuel consumption in the northeastern United States [*Lima et al.*, 2003]. The anoxic depositional setting of this location results in a laminated sediments that are conducive to reconstruction of historical records of combustion at both regional and local scales at high-temporal resolution [*Hites et al.*, 1980; *Lima et al.*, 2003, 2005b].

Several studies have focused exclusively on PAHs as tracers of condensed PyC by virtue of their ease of extraction and analysis, as well as information embedded in their distributions and isotopic compositions

regarding combustion sources [*Hites et al*., 1980; *Lima et al*., 2003; *Wakeham et al*., 2004; *Windsor and Hites*, 1979]. Other tracers of PyC are now also commonly employed, and some studies have yielded down-core profiles that contrast with those of PAHs [*Currie et al*., 2002; *Elmquist et al*., 2007; *Louchouarn et al*., 2007; *Muri et al*., 2006]. These discrepancies may be related to different modes of formation or transport of combustion products, or possibly to methodological artifacts. For example, PAHs are secondary products derived from condensation of initial low molecular weight combustion species [*Masiello*, 2004; *McBeath and Smernik*, 2009], with high-temperature combustion favoring the production of nonalkylated PAH assemblages [*Blumer*, 1976] that can coagulate to form soot-like structures [*Bockhorn*, 1994]. In contrast, charcoal comprises primary charred residues of biogenic materials. Compared to PAHs, charcoal and other products of incomplete combustion exhibit heterogeneous chemical characteristics (slightly charred to highly condensed; Figure S1 in the supporting information) [*Bird et al*., 2015; *Hammes et al*., 2007; *Wiedemeier et al*., 2015]. These two types of PyC represent end-members in a continuum of combustion products that vary in abundance as a function of the sources and conditions of production as well as subsequent fates [*Masiello*, 2004]. Available methods capture different parts of this PyC continuum, e.g., operationally defined fractions (graphitic black carbon (PyC_{GBC}), chemical thermal oxidation (PyC_{CTO}), and spheroidal carbonaceous particles [*Gélinas et al*., 2001; *Gustafsson et al*., 2001; *Rose*, 1994]), chemically defined (molecular) markers such as PAHs and benzene polycarboxylic acids (PyC_{BPCA}; supporting information Figure S1) [*Glaser et al*., 1998], or spectroscopic characteristics [*Baldock and Smernik*, 2002; *Lehmann et al*., 2005]. Application of a broad suite of methods is thus favored in order to constrain the abundance and characteristics of different PyC components (supporting information Table S1). Operationally defined fractions and chemically defined species also offer the potential to derive other information (e.g., carbon isotopic composition) that can be used to constrain the provenance of PyC.

Quantifying the heterogeneous mixtures of PyC in environmental matrices and constraining its sources is a challenging but a necessary step in order to understand this important component in the global carbon cycle. In the present study, we compare sedimentary profiles of PAHs in anoxic and laminated sediments from the Pettaquamscutt River basin, RI, USA [*Lima et al*., 2003], with those derived from application of three other methods used to quantify PyC at a bulk level aiming at to differentiate between local biomass burning in the catchment and regional-scale inputs from industrial sources of combustion. The goals were to (1) comprehensively quantify and characterize PyC, (2) compare the information on PyC gleaned from different combustion tracers and proxies, and (3) assess local and regional inputs of PyC.

2. Materials and Methods

2.1. Study Area

The Pettaquamscutt River estuary (Figure 1) is located in Washington County (southern Rhode Island, U.S.; 41.503816 and −71.450545) and drains a small watershed (35 km^2) with a north-south orientation [*Orr and Gaines*, 1973]. Present-day land cover mainly consists of oak tree forests, wetlands, and open waters [*Urish*, 1991] with approximately 30% as residential land. The geological setting underlying the Pettaquamscutt River basin is a Pennsylvanian (late Carboniferous) metasedimentary rock formation consisting of sandstone, conglomerate, schist, and graphite [*Hermes et al*., 1994].

Ocean water flooded the Pettaquamscutt estuary and the upper two basins about 1700 ± 300 years ago, leading to the formation of zoned circulation patterns with a vertical salinity gradient (10 ppt) that has caused oxygen depletion in basin bottom waters [*Hubeny et al*., 2009]. Since then surface sediments have been anoxic, limiting microbial decomposition [*Orr and Gaines*, 1973], and preventing bioturbation by macrofauna [*Hubeny et al*., 2009]. The water depth at the sampling location in the lower basin was 20 m, with the oxic/anoxic transition zone in the water column between 3.5 and 6 m and sulphidic waters below 6 m [*O'Sullivan et al*., 1997]. The high-temporal resolution sedimentary record stemming from the confined nature of the basin and the permanently anoxic conditions render it an ideal location for detailed historical reconstruction of PyC deposition.

2.2. Sampling

A series of freeze cores were collected in 1999 using a rectangular aluminum freeze corer (90 cm × 30 cm × 10 cm), dry ice, and methanol [*Lima et al*., 2003]. Sediment chronology was obtained from varve counting and ^{137}Cs and

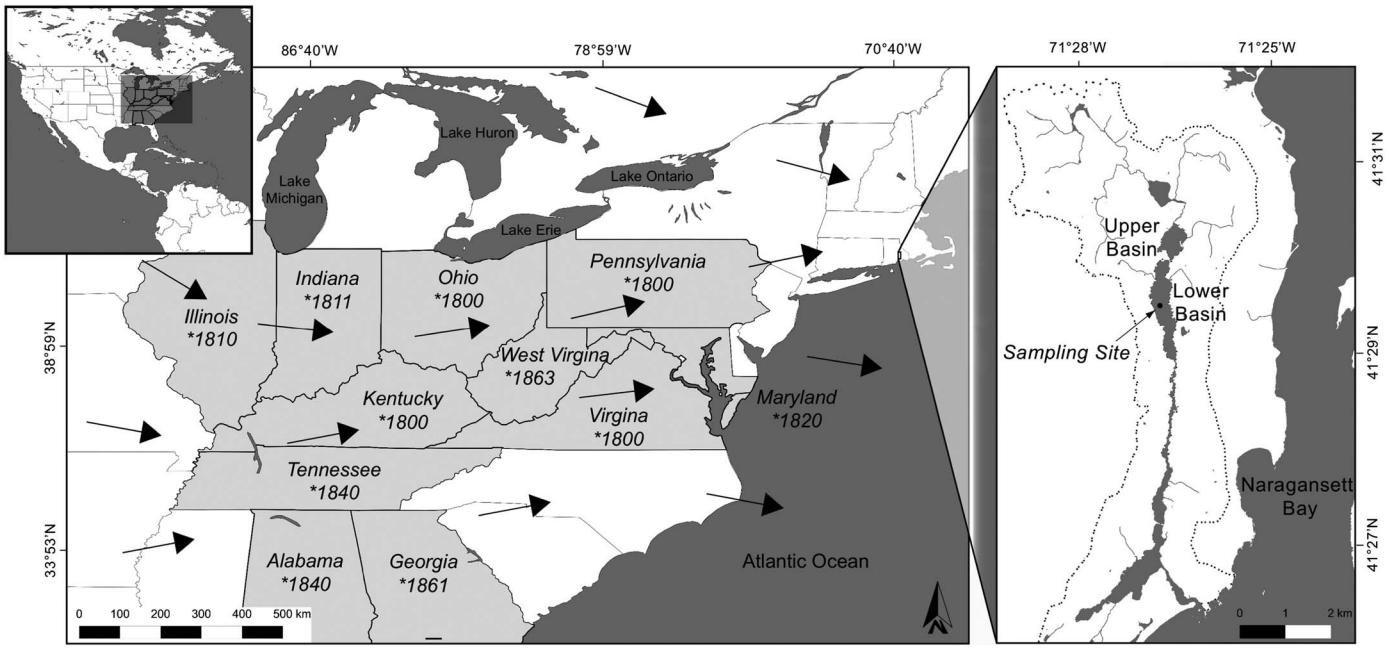

Figure 1. (left) Northeastern North America with major coal-producing states (light grey) and year (*) when coal production has started (U.S. Geological Survey) (http://pubs.usgs.gov/of/1997/of97-447/text.htm) and vector wind composite mean from NOAA/ESRL (1871–1998; http://www.esrl.noaa.gov/psd/cgi-bin/data/composites/plot20thc.v2.pl); (right) Pettaquamscutt River catchment (35 km^2), RI, U.S. showing boundaries of the drainage basin (dotted line) and the sampling location.

^{210}Pb profiles using the constant rate of supply model [*Lima et al.*, 2005b]. In short, gamma spectrometry was used to detect ^{210}Pb (46.5 keV), ^{226}Ra (351 keV), and ^{137}Cs (661 keV). Excess ^{210}Pb was calculated from total ^{210}Pb and supported ^{210}Pb activity. Limit of detection was 0.040 Bq for excess ^{210}Pb and 0.004 Bq for ^{137}Cs [*Lima et al.*, 2005b]. Sediment chronology (1999 ± 0 to 1855 ± 7) was compared for four key horizons (Chernobyl peak: 1987 ± 1, maximum fallout: 1963 ± 2, and hurricane-sand layers: 1954 ± 3, 1938 ± 4) [*Lima et al.*, 2005b]. Additionally, varve counting with radiograph images allowed extension of the sediment chronology back to 1750. Except for measurements of trace metals and PAHs, all analyses were carried out on four additional cores that were aligned via x-radiograph analysis (to cross-correlate laminae), sliced, freeze dried, combined, and subsequently stored in precombusted glass jars.

An elemental analyser (Fisons 1108) was used to determine TOC and nitrogen contents in the samples. In short, 2 mg dry sediment was weighed in silver capsules and acidified with 20 μL 2 N hydrochloric acid (HCL) under vacuum, dried in the oven (50°C), and analyzed [*Lima*, 2004]. Sediment in situ densities were calculated from dry densities measured using a 2 mL specific gravity bottle and porosity retrieved from weight percent of water [*Lima*, 2004]. The four PyC records differ in their temporal resolution. The PyC_{PAH} record comprises 77 sample depths to track rapid changes in U.S. fuel combustion; the PyC_{BPCA} record consists of 40 depths, and those for PyC_{CTO}, PyC_{GBC} comprises 22 depths. The higher number of PyC_{BPCA} measurements was made to assess the coarser records.

2.3. Polycyclic Aromatic Hydrocarbons

PAHs are a group of chemical compounds consisting of fused benzene rings [*Mumtaz and George*, 1995] and in this study we focus on nonalkylated PAHs that represent intermediates in soot-like particle formation [*Blumer*, 1976]. The procedure for acquiring the high-resolution PAH record was previously described [*Lima et al.*, 2003]. Briefly, 0.5–1.5 g dry sediment was spiked with PAH internal standards and extracted by pressurized fluid extraction (1000 psi; 100°C) with acetone and hexane (1:1). The aromatic hydrocarbon fraction was measured on an Agilent 6890/5970 GC/MSD System operating at 70 eV in selective ion monitoring mode using a DB-XLB capillary column to separate compounds [*Lima et al.*, 2003]. Measurement precision is ±5% and the recovery of standards spiked into each sample is 84.9 ± 9.9% [*Lima*, 2004]. Total pyrogenic PAH concentrations reported included the following combustion-related species: fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene,

benzo[*a*]pyrene, benzo[e]pyrene, dibenz[*a*,*h*]anthracene, indeno[*1*,*2*,*3-c*,*d*]pyrene, benzo[*g*,*h*,*i*]perylene, coronene, and together are defined here as PyC_{PAH}.

2.4. Benzene Polycarboxylic Acids

Benzene polycarboxylic acids (BPCAs) are molecular markers for PyC that are formed during a laboratory procedure for oxidative degradation of condensed polycyclic aromatic centers, thereby serving as measures for PyC [*Glaser et al*., 1998]. BPCAs were obtained from the sediments by thermal digestion (170°C, 8 h) with nitric acid and quantified with liquid chromatography [*Dittmar*, 2008; *Glaser et al*., 1998; *Wiedemeier et al*., 2013] using an Agilent 1290 infinity high-performance liquid chromatography system and Agilent Poroshell 120 column. Trimellitic acid (Fluka 92119), hemimellitic acid (Aldrich 51520), pyromellitic acid (Fluka 83181), pentacarboxylic acid (Aldrich S437107), and mellitic acid (Aldrich M2705) were used as external standards in a seven-point calibration curve (2–200 ng μL^{-1}). The measurement precision of PyC_{BPCA} is, on average, ±5% [*Wiedemeier et al*., 2013]. For stoichiometric reasons, PyC_{BPCA} accounts for a maximum of about 25% of the total PyC [*Brodowski et al*., 2005; *Schneider et al*., 2011].

2.5. Chemical Thermal Oxidation

This methodological approach targets forms of PyC that exhibit a high degree of condensation, such as soot [*Gustafsson et al*., 1997, 2001]. In short, dried (60°C) and finely ground sediments were weighed (about 200 μg C) in Ag capsules. Then inorganic carbon was removed in situ by microacidification with liquid 1 N HCl and dried at 60°C again. Residual sediment was then spread in a thin layer on a precombusted watch glass and heated to 375°C in a programmable oven (Fisher Scientific IsoTemp) for 24 h in the presence of excess oxygen. The remaining carbon, subsequently measured with an elemental analyser (Fisons 1108), was defined as PyC_{CTO}. Generally, the precision of measurements is reported with a relative standard deviation of 1–3% [*Gustafsson et al*., 1997]. PyC_{CTO} concentrations may be altered due to additional charring of labile organic matter during the isolation procedure [*Accardi-Dey*, 2003; *Nguyen et al*., 2004] and can be overestimated by as much as 3 orders of magnitude [*Gélinas et al*., 2001].

2.6. Graphitic Black Carbon

Measurement of graphitic black carbon (PyC_{GBC}) is based on a modified PyC_{CTO} protocol and aims at reducing the potential formation of condensation products resulting from charring of non-PyC compounds during isolation [*Reddy et al*., 2002] and thus preventing an overestimation of PyC in environmental matrices. The sediment samples were first treated with 1 N HCl and 10% HF, then hydrolysable organic matter was stepwise removed with 2 N, 4 N, and 6 N trifluoroacetic acid [*Gélinas et al*., 2001]. The resulting material was then thermally treated as for the PyC_{CTO} method, with remaining carbon defined here as PyC_{GBC}. The thermal oxidation including the chemical pretreatment shows a coefficient of variation of $<1\%$ [*Gélinas et al*., 2001]. However, the chemical pretreatment enhances the physical loss of sample material of about 15% [*Gélinas et al*., 2001].

2.7. Data Analysis

PyC_{PAH} when absorbed to other materials can be transported through the atmosphere before deposition and temporary storage in intermediate reservoirs [*Dachs and Eisenreich*, 2000; *Koelmans et al*., 2006; *Wozniak et al*., 2011]. We assume that particulate PyC can subsequently be transported from soils in the catchment to the sedimentary archive via surface runoff or soils erosion. Aquatic sediments and associated PyC may also experience short-term storage in sediments on the basin flanks before eventual accumulation in the depocenter. *Lima* [2004] revised the ^{210}Pb chronology for an excess accumulation from the basin periphery and determined a focusing factor of 1.3 based on the atmospheric ^{210}Pb inventory measured in New Haven, CT (38.6 dpm cm^{-2}) [*Turekian et al*., 1983], and the vertically integrated unsupported ^{210}Pb calculated for Pettaquamscutt River sediments (51.6 dpm cm^{-2}) [*Lima*, 2004]. To account for this phased particle (and associated PyC) deposition, translocation, and accumulation, we applied a 20 year moving average on PyC_{PAH}, PyC_{BPCA}, PyC_{CTO}, and PyC_{GBC}. This is consistent with a deposition delay of nearly two decades indicated by the records of ^{137}Cs [*Lima et al*., 2005b] for the same sediments.

Similarities among the different PyC records were also assessed statistically (Figure 2e) via computing distances for cross correlations of the four PyC records [*Montero and Vilar*, 2014]. Using classical

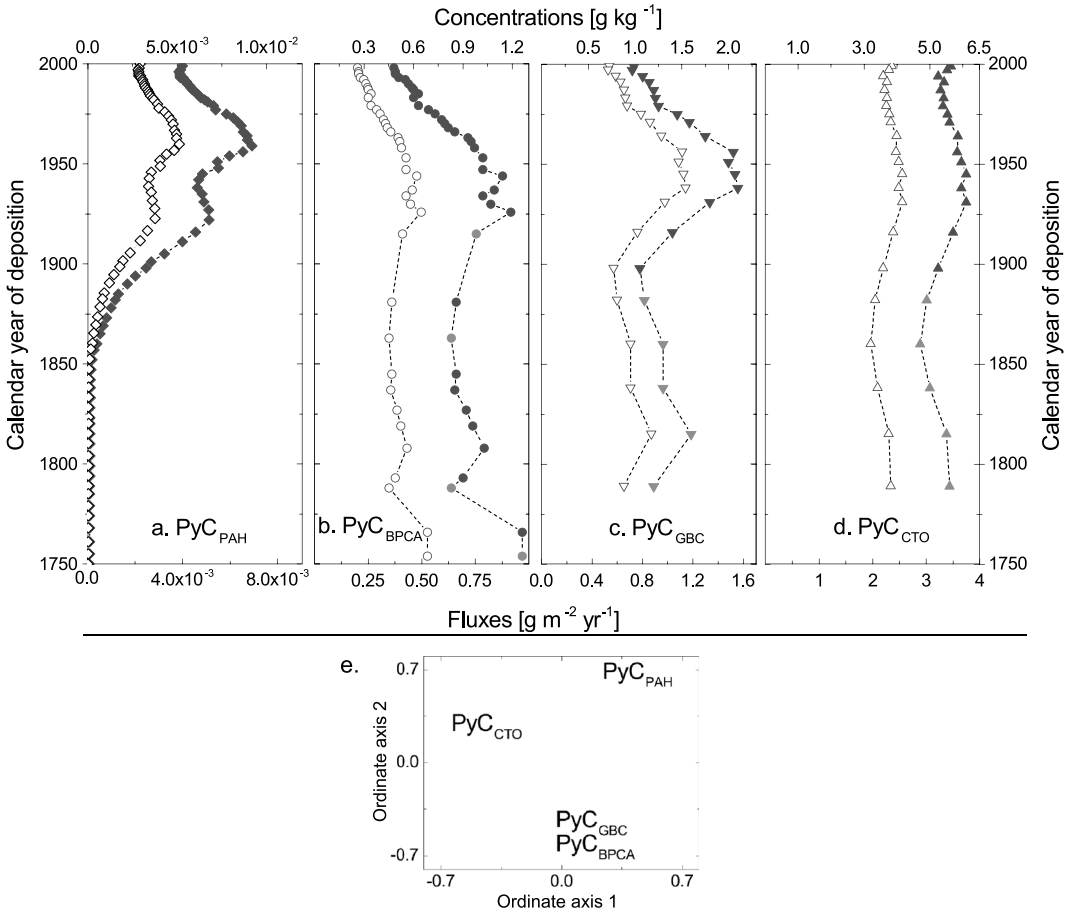

Figure 2. (a–d) Four records on PyC concentrations (closed symbols) and fluxes (open symbols) of the Pettaquamscutt River sediments, RI, U.S. Data are displayed as 20 year moving averages (dark grey) and single data points (light grey). (e) Similarities between the four PyC records, expressed as distances in a two-dimensional coordinate system. Entries in proximity to each other are more similar than distant ones.

multidimensional scaling [*Cox and Cox*, 2001], these distances were represented in two dimensions. Missing data points in the records were replaced with values from linear interpolations prior to these calculations.

3. Results

A comprehensive examination of the PyC_{PAH} record (1750–1999) is described by *Lima et al.* [2003]. Individual values of PyC_{BPCA} (1754–1998), PyC_{GBC} (1789–1999), and PyC_{CTO} (1789–1999), as well as data on nitrogen content of residues can be found in Table S3 and S4 (supporting information). Corresponding 20 year moving averages of the four PyC methods are shown in Figures 2a–2d. We also calculated fluxes, derived from PyC concentrations (g kg^{-1}), deposition rates (g m^{-2} yr^{-1}), and in situ densities (kg m^{-3}). As PyC concentrations are reported more frequently in literature, and since fluxes exhibit very similar patterns, we focus on the former values in discussion of the data.

3.1. Polycyclic Aromatic Hydrocarbons

Total PyC_{PAH} concentrations vary between 0.00008 g kg^{-1} (mid-1700s) and 0.0113 g kg^{-1} (1956 ± 3). Prior to 1840s PyC_{PAH} concentrations remain at background values (≤0.000136 g kg^{-1}), and then increase, concomitant with an increasing consumption of fossil fuels at the onset of industrialization. A first peak in PyC_{PAH} concentrations appears in 1927 ± 4 (0.00676 g kg^{-1}). After a sudden drop during the Great Depression years (1930s), PyC_{PAH} concentrations increase again and reach an overall maximum (0.00919 g kg^{-1}) in 1959 ± 3. Thereafter, the concentrations tend to decrease, punctuated by another small peak prior to the

Organization of Petroleum Exporting Countries (OPEC) oil embargo in 1973 ± 2, and reach a minimum (0.0051 g kg^{-1}) in 1996 ± 1. The slight increase (0.0007 g kg^{-1}) between 1996 ± 1 and 1999 ± 0 may reflect urbanization of the local area [*Hubeny et al*., 2009].

The PyC_{PAH} record parallels the record of industrialization of the northeastern United States during the nineteenth and twentieth centuries, particularly with respect to the usage of fossil fuels. The relative proportions of 15 different PAHs (and corresponding source diagnostic ratios) indicate minor contributions of petroleum-associated hydrocarbons throughout the entire record, implying that combustion is the primary source of PAHs [*Lima et al*., 2003]. Moreover, the PAH are considered to be predominantly supplied via atmospheric deposition rather than urban surface runoff as indicated by the absence of an unresolved complex mixture in the sample matrix [*Lima et al*., 2003].

3.2. Benzene Polycarboxylic Acids

PyC_{BPCA} concentrations vary between 0.25 g kg^{-1} (1993 ± 1) and 1.43 g kg^{-1} (mid-1700s). They exhibit a slight decrease from the earliest portion of the record, reaching a broad minimum in the mid-1800s (0.83 g kg^{-1}), before returning to a second maximum in 1920s (1.40 g kg^{-1}). Concentrations then tend to decrease monotonically approaching the end of the twentieth century (0.48 g kg^{-1}).

3.3. Chemical Thermal Oxidation

Concentrations of PyC_{CTO} vary between 4.70 g kg^{-1} (1860 ± 7) and 6.10 g kg^{-1} (1931 ± 4). In the late eighteenth century, concentrations of PyC_{CTO} exhibit intermediate values (5.60 g kg^{-1}) before decreasing slightly until the 1860s (4.70 g kg^{-1}). Concentrations then exhibit a systematic increase to a maximum in 1930s (6.10 g kg^{-1}). Thereafter the PyC_{CTO} record remains relatively constant without any distinct trend until the end of the twentieth century. Nitrogen concentrations (supporting information Table S4) in the thermal residues are uniform (0.9–1.0 g kg^{-1}), and corresponding C/N ratios of PyC_{CTO} vary between 5.1 and 7.0. These systematically low C/N ratios (supporting information Figure S4) point toward the formation of artifacts due to charring of nitrogen-containing nonpyrogenic macromolecules during the analysis [*Accardi-Dey*, 2003]. Thus, we do not discuss the results of PyC_{CTO} further.

3.4. Graphitic Black Carbon

PyC_{GBC} concentrations vary from 0.97 g kg^{-1} (1997 ± 1) to 2.10 g kg^{-1} (1938 ± 4). PyC_{GBC} concentrations increase from 1.20 g kg^{-1} in the late eighteenth century to 1.60 g kg^{-1} in early nineteenth century. Concentrations then gradually decline to a minimum of 1.05 g kg^{-1} at the end of nineteenth century before increasing again to a broad maximum in the middle twentieth century (2.10 g kg^{-1}). PyC_{GBC} concentrations then markedly decrease toward the present-day (0.99 g kg^{-1}). Nitrogen contents (supporting information Table S4) in the thermal residues vary between 0.03 and 0.08 g kg^{-1}, and corresponding C/N ratios of PyC_{GBC} vary between 16.3 and 48.8. Compared to PyC_{CTO} these wider and generally higher C/N ratios indicate lesser production of charring artifacts during the isolation of PyC_{GBC}.

4. Discussion

There are relatively few reported studies in which historical records of combustion have been developed based on more than one tracer of PyC. The comparability of different PyC approaches has, up to now, mainly been reported for standard materials, e.g., *Currie et al*. [2002], *Hammes et al*. [2007], and *Roth et al*. [2012]. In particular, investigations that compare and contrast PyC records in coastal sediments are scarce [*Elmquist et al*., 2007; *Louchouarn et al*., 2007; *Muri et al*., 2006], yet understanding transport and sequestration of PyC in these settings is crucial for developing insights into global-scale biogeochemical cycles of pyrogenic and other forms of reduced (organic) carbon.

Distinctive deposition patterns of PyC in continental shelf sediments of the northeastern United States have been shown previously, e.g., *Gustafsson and Gschwend* [1997; 1998], *Hites et al*. [1980], and *Windsor and Hites* [1979]. Prevailing (south)westerly winds transport particulate PyC over long distances and link the coastal areas with industrial and urban regions inland.

4.1. Fidelity and Representativity of PyC Data

While varying sensitivity to different PyC sources and characteristics complicates assessment of the comparability of the four PyC approaches, information derived from these approaches sheds light on dynamics of different components of the PyC continuum, and collectively, they offer more comprehensive insights into this important carbon pool. In this regard, the Pettaquamscutt PyC_{PAH} record mirrors the overall history of energy consumption in the northeastern United States, faithfully documenting key episodes and transitions in usage of different types of fuel [*Lima et al*., 2003]. However, PAHs represent trace PyC constituents, as is evident from their concentrations, and so it is important to compare profiles with other proxies that are more representative of bulk PyC (PyC_{BPCA} and PyC_{GBC}).

The four PyC methodologies used in this study are assumed to capture different portions of the combustion continuum [*Hammes et al*., 2007]. For the Pettaquamscutt River record, each PyC proxy yields different concentrations (Figure 2). These discrepancies likely reflect the different analytical windows inherent in each measurement approach, modes of PyC formation during burning/combustion (e.g., charring versus condensation reactions), and also methodological artifacts.

4.2. PyC Contents in Coastal Sediments

PyC_{BPCA} concentrations in the Pettaquamscutt River sediments are similar to those found in coastal surface sediments in SW Spain (0.33–1.48 g kg^{-1}; $n = 4$) [*De la Rosa et al*., 2011] or (0.1–2.3 g kg^{-1}; $n = 15$) [*Sánchez-García et al*., 2013] but higher than those found in the northeast Pacific Ocean sediments (0.5–1.1 g kg^{-1}; $n = 14$) [*Coppola et al*., 2014].

For PyC_{GBC}, concentrations are higher compared to those reported for a terrestrial nearshore to marine offshore transect at Washington coast (0.09–0.71 g kg^{-1}) [*Dickens et al*., 2004] but similar to sediments from Lake Washington (0.22–0.58 g kg^{-1}; $n = 20$) [*Wakeham et al*., 2004] and from the inner shelf of SW Iberian Peninsula (0.26–1.12 g kg^{-1}; $n = 4$) [*De la Rosa et al*., 2011].

The high concentrations of PyC_{PAH}, PyC_{BPCA}, and PyC_{GBC} in the Pettaquamscutt River sediments are comparable to other archives that are either downwind of heavy industry or nearby large industrial areas.

4.3. Decoupled Records

PyC_{PAH} concentrations are 2 orders of magnitude lower than the other methods applied in this study. Nonetheless, PyC_{PAH} have been extensively studied due to the carcinogenic properties of specific PAHs [*Mumtaz and George*, 1995] and the PyC source information embedded in their distribution [*Currie et al*., 1997; *Rogge et al*., 1993]. Thus, although they are trace PyC constituents, it is important to determine temporal variations in their deposition, as well as their origin.

Notably, PyC_{PAH} concentrations remain low (natural background levels) during the preindustrial era and then reach their maximum during the second half of the twentieth century. The overall trend in PyC_{PAH} concentrations parallels the use of fossil fuels in the northeastern United States. Variations in PyC_{PAH} concentration reflect changes in the type of fuel (coal and oil) and combustion processes (e.g., use of catalytic converters) [*Lima et al*., 2003] and are superimposed on a constant increase in the consumption of fossil fuels during the industrial era [*Lima et al*., 2003, 2005a]. In contrast, the results of the "bulk" PyC approaches (PyC_{BPCA} and PyC_{GBC}) vary only slightly in terms of concentration and show broadly parallel down-core variations, implying that they track an important yet distinct component of PyC. Determining the causes of this apparent decoupling of records for different PyC tracers is crucial for a comprehensive quantification of this key carbon pool, as well as for informed interpretation of combustion records.

Within the combustion continuum, PyC can also be comprised of residues produced at low temperature (wood burning) and thus at a lower combustion efficiency. Such residues typically consist of larger PyC particles characterized by a low to intermediate degree of condensation [*Masiello*, 2004]. The other end of the PyC spectrum derives from condensation reactions in the gas phase during high-temperature combustion of fossil fuels and mainly yields PAH and other fine-carbon particles with a high degree of condensation, including soot.

We examined correlations among the four PyC records in order to further assess their degree of similarity/dissimilarity (Figure 2e). This revealed coherence between PyC_{BPCA} and PyC_{GBC} records, but not

in that of PyC_{CTO}, while all three are clearly decoupled from the PyC_{PAH} record. Moreover, different modes PyC productions are evident in the data. The regional-scale history of fossil-fuel combustion since industrialization is echoed in the PyC_{PAH} record. In contrast, the local wood burning practices appear to manifest themselves in PyC_{BPCA} and PyC_{GBC} records, particularly during preindustrial times when such practices were most pronounced and combustion of fossil fuels had yet to begin.

4.4. Origin and Transport Pathways

There are several lines of evidence to suggest that the Pettaquamscutt River sediments integrate emissions and deposition on a regional scale as chronicled in the PyC_{PAH} record and in a Pb isotope-based record of combustion sources [*Lima et al*., 2003, 2005a, 2005b]. Mining and industrial activities in the Upper Mississippi Valley (about 1600 km westward of our study area) and Pennsylvania coal region (about 450 km west-southwest of our study area) [*Census*, 1975] were considered primary sources of the signals observed in the Pettaquamscutt River basin. Wind vector data (Figure 1) lend support for this interpretation of PyC_{PAH} provenance in the northeastern United States [*Golomb et al*., 2001; *Lima et al*., 2005a].

Given that the PyC_{PAH} record appears to reflect long-range atmospheric transport, the sharply contrasting PyC_{BPCA} and PyC_{GBC} down-core profiles must trace different PyC source(s) and/or modes of supply to Pettaquamscutt River basin sediments. In particular, the high abundance of PyC_{BPCA} and PyC_{GBC} in sediments deposited prior to the industrial era, as well as their relatively modest variations throughout the record, indicates different source inputs. We infer that the latter derives from inputs stemming from runoff and soil erosion in the Pettaquamscutt watershed and that the corresponding down-core record therefore reflects the local land use history. The Pettaquamscutt River catchment was deforested during the late seventeenth century and then used as agricultural land until the beginning of eighteenth century [*Hubeny et al*., 2009]. Land under cultivation gradually decreased by 88% from 1850 to 1969 [*Census*, 1975], eventually accounting for only 4.1% land usage at the end of the twentieth century [*Widmann*, 2002]. Widespread deforestation has been accompanied by extensive burning, promoting accumulation of charcoal residues in soils [*Santín et al*., 2015]. Mobilization of burning residues via runoff and bank erosion, potentially also exacerbated by agricultural practices such as plowing, would eventually result in delivery of particulate PyC to river basin sediments. This process of mobilization and lateral transfer could have continued long after the land use change occurred [*Whitlock and Larsen*, 2001]. Formerly deforested areas underwent regeneration until middle twentieth century. Since then, timber stock has further increased by a factor of 3 even though the forested area declined by ~5% due to increasing population density [*Widmann*, 2002]. Local erosion of particulate PyC is probably ongoing, albeit at a lower level.

In preindustrial times, PyC must have been supplied predominantly via local surface runoff and erosion processes. With the onset of industrialization, and particular with extensive use of coal for fuel, local PyC inputs have been augmented by atmospheric supply of PyC residues from upwind sources (e.g., Pennsylvania). This additional source of PyC may be responsible for the relatively (compared to changes in PyC_{PAH} concentrations) modest increase in PyC_{BPCA} and PyC_{GBC} concentrations from middle nineteenth century to the first half of the twentieth century. During this time period all four PyC records reach their maxima, implying that atmospheric deposition must have influenced overall PyC sedimentary burdens. Subsequent to the 1970s, with the exception of a brief maximum in PyC_{BPCA} in the 1980s that may reflect a surface runoff (storm) event (supporting information Table S2), all records show a decline in concentration that parallels the implementation of liquid fuels (more efficient conversion to energy and carbon dioxide) and improved controls on particle emissions.

4.5. Implications—Combining Complementary Analytical Tools

The observations resulting from the present study suggest that complementary approaches are required for comprehensive reconstruction of past combustion practices and fire history of a watershed from sedimentary records. In particular, it is important to use methods that capture both charcoal and soot PyC, as well as other components of the combustion continuum. The PyC_{PAH} mainly traces fossil-fuel combustion, whereas the other tools applied here appear to primarily reflect biomass burning residues. Molecular markers can provide qualitative information on PyC source (PyC_{PAH}) and the degree of condensation (PyC_{BPCA}); however, quantitative assessments of PyC for the purpose of constraining budgets require use of proxies such as PyC_{BPCA} and

PyC_{GBC} that reflect a larger part of the PyC continuum (slightly charred to highly condensed PyC) in combination with further approaches to constrain PyC sources (e.g., radiocarbon analysis).

5. Conclusions

This study sheds new light on the provenance and mode of supply of PyC accumulating in aquatic sediments. Comparison of down-core concentration profiles of four different proxies measured at high-temporal resolution shows that PyC_{PAH} are strongly decoupled from those of the other PyC methods, while PyC_{BPCA} concentration profiles parallel those from the PyC_{GBC} method.

The PyC_{PAH} record mirrors the general increase in production and consumption of fossil fuels brought on by the industrial revolution, with atmospheric transport serving as the primary vector of PyC_{PAH} supply from upwind source regions. In contrast, the PyC_{BPCA} and PyC_{GBC} records likely reflect local land use changes (deforestation, agriculture, and urbanization) that resulted in PyC accumulation in and mobilization from soils within the Pettaquamscutt river watershed. Regional-scale supply and atmospheric deposition of PyC combustion residues appear to be much less important in terms of overall PyC burdens, with only a minor increase in overall PyC quantities accompanying the peak in PyC_{PAH} deposition in the middle twentieth century. All PyC records exhibit a marked decline during the latter half of the twentieth century, concomitant with the use of cleaner fuels and the advent of more stringent emissions regulations.

This study highlights the need for careful consideration of both PyC source characteristics and transport processes in deciphering past records of combustion and in development of accurate budgets of PyC production and deposition on local to regional scales. Our findings clearly show that different methodological approaches track different portions of the PyC continuum. Further approaches, such as compound-specific radiocarbon analysis, are needed to resolve and quantitatively apportion PyC signatures accumulating in environmental matrices such as sediments.

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